

## Cave atmosphere: A guide to calcification and a methane sink

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### Cave Environment

Studies of cave environments and speleothem growth are an important step towards quantitative speleothem palaeoclimate interpretation. Net accumulation of CaCO<sub>3</sub> (speleothem growth) requires a perturbation to Gas-Aqueous-Solid equilibrium conditions in the cave environment (Aq. chem., T, P, pCO<sub>2</sub>). The largest equilibrium change in a ventilated cave environment causing speleothem growth is fluctuating pCO<sub>2</sub> as a response to the cave air exchange, driven by external temperature.

An intense 3-week field campaign in May 2008 (winter) using an FTIR spectrometer continuously measured (5 min) trace gases (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) H<sub>2</sub>O and δ<sup>13</sup>C<sub>CO2</sub>. Simultaneous drip-water pH, air flow, temperature, pressure, and relative humidity was logged by sensors in the cave together with external rainfall, temperature, pressure, and relative humidity. Drip water was sampled twice daily, coinciding with CO<sub>2</sub> maxima and minima, for dissolved inorganic carbonate DIC, δ<sup>13</sup>C<sub>DIC</sub>, dissolved organic carbonate DOC, δ<sup>13</sup>C<sub>DOC</sub>, alkalinity, anions, and cations. Further spot samples were taken for drip-water stable isotopes, <sup>14</sup>C<sub>DIC</sub>, and <sup>3</sup>H.

Low pCO<sub>2</sub> in the morning cave air causes rapid speleothem growth with CO<sub>2</sub> exsolved to the cave atmosphere lowering drip-water pH. pCO<sub>2</sub> increases to an evening maxima and slows speleothem growth before early morning T induced ventilation decreases pCO<sub>2</sub>. δ<sup>13</sup>C<sub>CO2</sub> has an antithetic relationship with CO<sub>2</sub>, with low pCO<sub>2</sub> morning air the highest δ<sup>13</sup>C<sub>CO2</sub> at -8 ‰ PDB. A Keeling analysis of end-member component mixing reveals the proportion of external air drawn into the cave and CO<sub>2</sub> produced from speleothem formation through the diurnal cycle.

Methane concentration in cave air also cycles through a diurnal pattern, negatively correlated with CO<sub>2</sub>. The methane concentration ranges from normal atmospheric 1700 ppb to <200 ppb and cycles 1000 ppb in only a few hours. Methane consumption is very rapid, suggesting a biogeochemical mechanism.

## How Mo isotopes fractionate during adsorption to Mn and Fe oxyhydroxides

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Several studies have reported metal isotope fractionations during adsorption of metals to minerals or cell membranes, but few have identified the molecular-scale mechanisms driving the observed effects. Using EXAFS analysis of experimental samples and density functional theory (DFT), we have determined how Mo isotopes fractionate during adsorption to Mn and Fe oxyhydroxides.

We reported previously a large Mo isotope fractionation during adsorption to birnessite, a poorly-crystalline Mn oxyhydroxide (Δ<sup>97/95</sup>Mo ~1.8‰; [1,2]). EXAFS analysis revealed that Mo adsorbs as a polynuclear species, e.g., Mo<sub>6</sub>O<sub>19</sub><sup>2-</sup>, with Mo in distorted octahedral coordination. Although present at minute quantities in solution in our experiments (<10<sup>-40</sup> M), polymolybdate is the predominant adsorbed complex on birnessite likely because the arrangement of oxygens matches that on the birnessite surface very closely. DFT calculations of fractionation between the main solution species, MoO<sub>4</sub><sup>2-</sup>, and Mo<sub>6</sub>O<sub>19</sub><sup>2-</sup> agree extremely well with experimental results from 1° to 50°C.

We also measured a moderate Mo isotope fractionation during adsorption to ferrihydrite (Δ<sup>97/95</sup>Mo ~0.8‰; [3]). Here EXAFS spectra indicate no polynuclear Mo species at the surface. Rather, Mo is likely present as four different complexes, two with Mo in tetrahedral and two with Mo in distorted octahedral coordination. The tetrahedrally coordinated Mo is likely unfractionated from solution, while the octahedrally coordinated Mo is enriched in lighter isotopes, thus explaining the moderate fractionation.

Our result demonstrates the critical importance of the identity of sorbed species in governing metal isotope effects during adsorption, in this system and likely in general.

[1] Barling & Anbar (2004) *EPSL* **217**:315. [2] Wasylenki et al. (2008) *Geochim. Cosmo. Acta.* **72**:5997. [3] Wasylenki et al. (2008) *Astrobiology* **8**(2), 8-26-O.